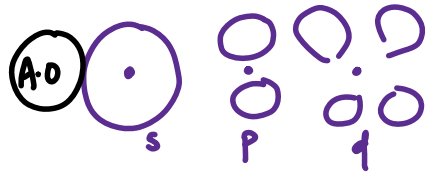
Molecular orbital theory

Thursday, 29 September 2022 14:26

Molecular orbital theory (MOT)

BASED on following assumptions :—

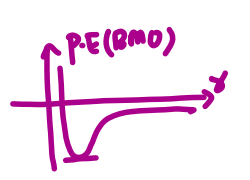
1) When two atoms approach each other, their atomic orbitals (A.O) lose their identity and mutually overlap to form new orbitals called molecular orbitals (M.O)
2) The MOs are polycentric (→ no. of nuclei > 1) and are associated with the nuclei of all the atoms making molecule.
3) Only A.Os of about the same energy and same symmetry interact significantly. → positive overlap (Constructive overlap)
4) No. of A.Os overlapped = No. of M.Os formed
5) Two type of M.Os are formed
   - (i) Bonding M.Os → By constructive overlap of A.Os (+ve overlap) ⇒ e⁻ density b/w nuclei ↑es ⇒ attrⁿ ↑es, PE reaches min
   - (ii) Antibonding M.Os → By destructive overlap of A.Os (negative overlap) ⇒ e⁻ density b/w nuclei ↓es ⇒ replⁿ b/w Nuclei ↑es; P.E ↑ with dec in internuclear distance. Node appear
6) Like A.O are filled; Similarly M.Os are filled using AHP Rules. (Aufbau, Hund, Pauli)

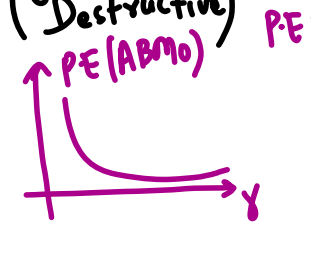


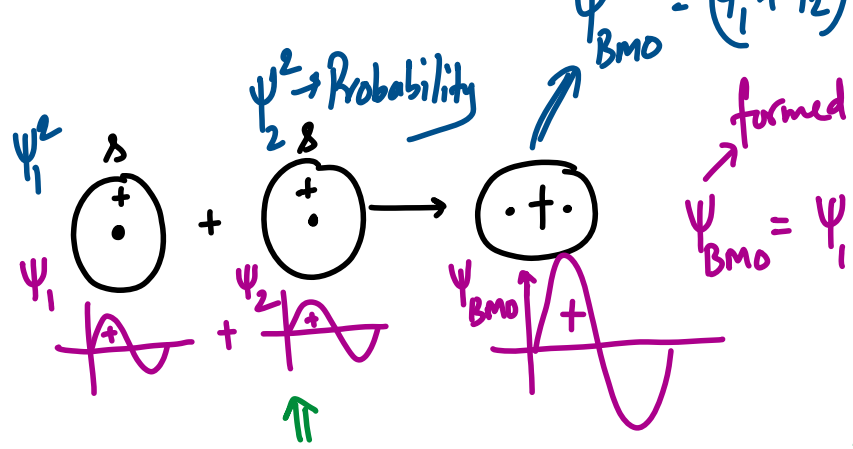
MO ⇒ σ, σ*, π, π*

BMO ← (σ, π) ← By +ve overlap (Same phase overlap) (Const.) — attrⁿ; P.E ↓ & reach min

ABMO ← (σ*, π*) ← By −ve overlap (opp. phase overlap) (Destructive) — P.E ↑, replⁿ





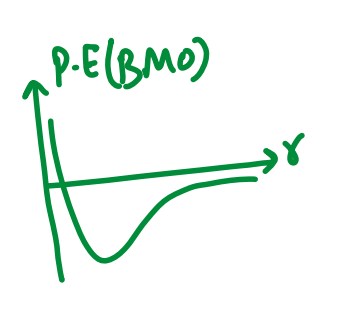


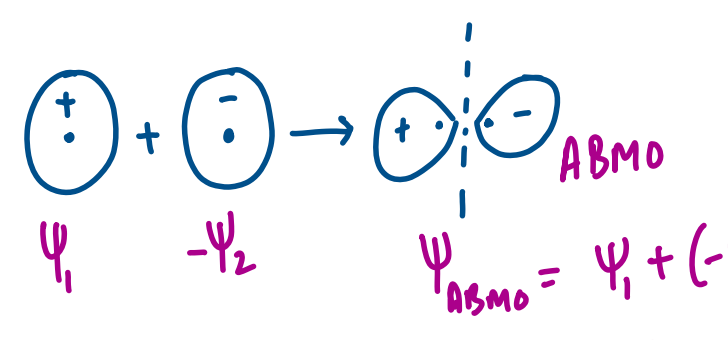
$$\psi_{BMO}^2 = (\psi_1+\psi_2)^2 = \psi_1^2+\psi_2^2+\boxed{2\psi_1\psi_2}$$ → integral overlap

$$\boxed{\psi_{BMO}^2 > \psi_1^2+\psi_2^2}$$

formed by Linear Combinatⁿ of A.O (LCAO)

$\psi_{BMO} = \psi_1 + \psi_2$

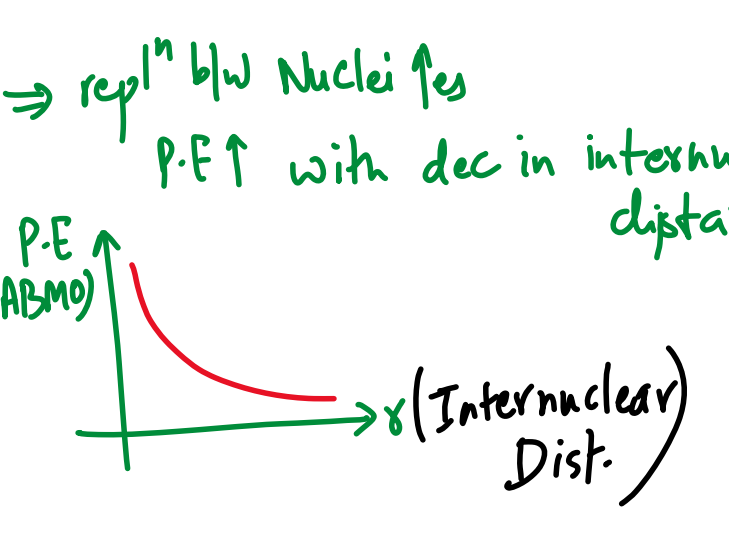




$\psi_{ABMO} = \psi_1 + (-\psi_2)$

Prob. of getting e⁻ in ABMO ⇒ $\psi_{ABMO}^2 = \psi_1^2+\psi_2^2-\boxed{2\psi_1\psi_2}$

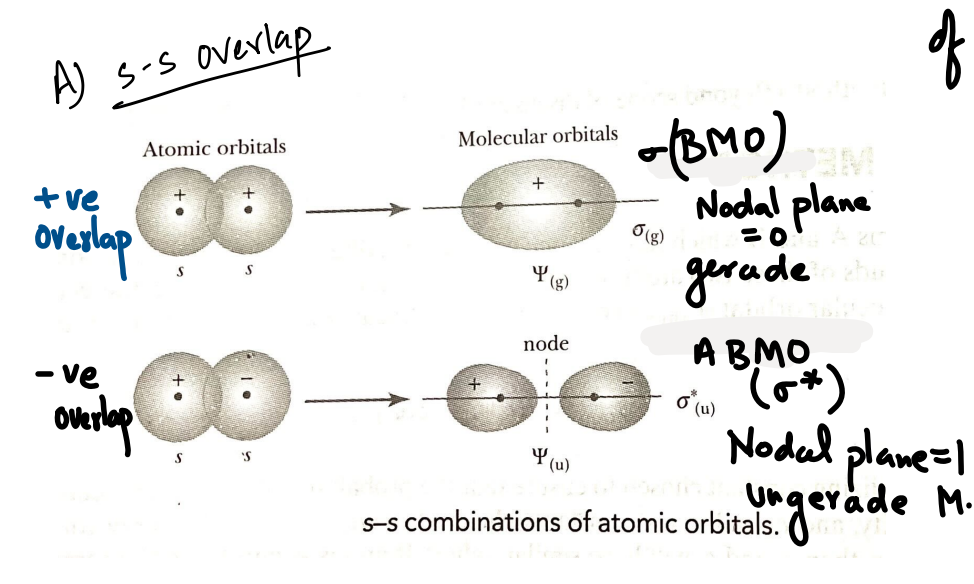
Prob. $$\boxed{\psi_{ABMO}^2 < \psi_1^2+\psi_2^2}$$



7) Formation of M.O by (LCAO) Method

LCAO → Linear Combination of A.O

A) s-s overlap



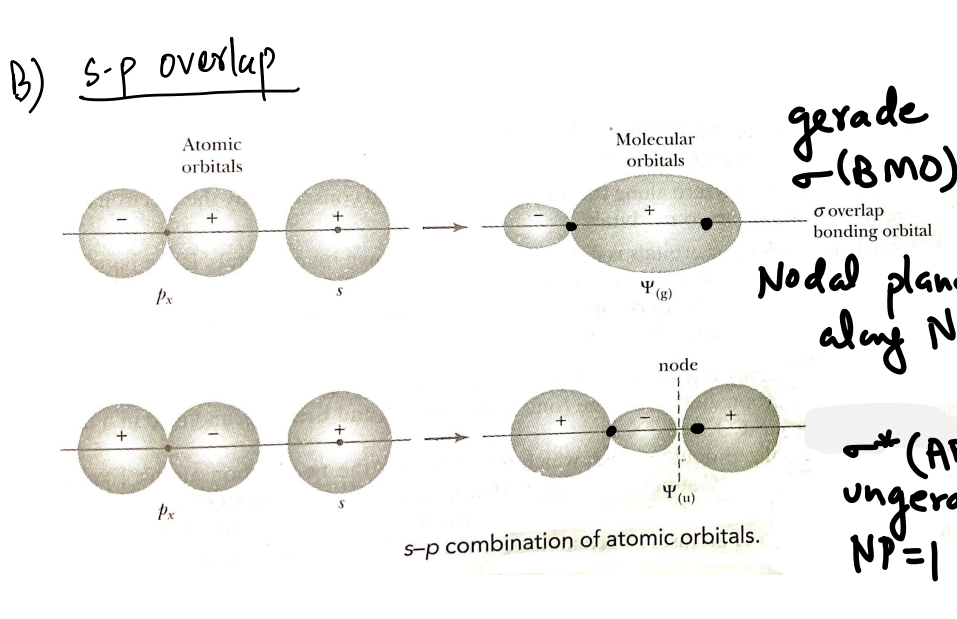
s–s combinations of atomic orbitals.

BMO	ABMO
g ⇐ σ	σ* ⇒ u (Ungerade)
u ⇐ π	π* ⇒ g (gerade)

gerade ⇒ no. of nodal plane (b/w nuclei or along Nuclei) even ⇒ 0, 2, 4 - - -

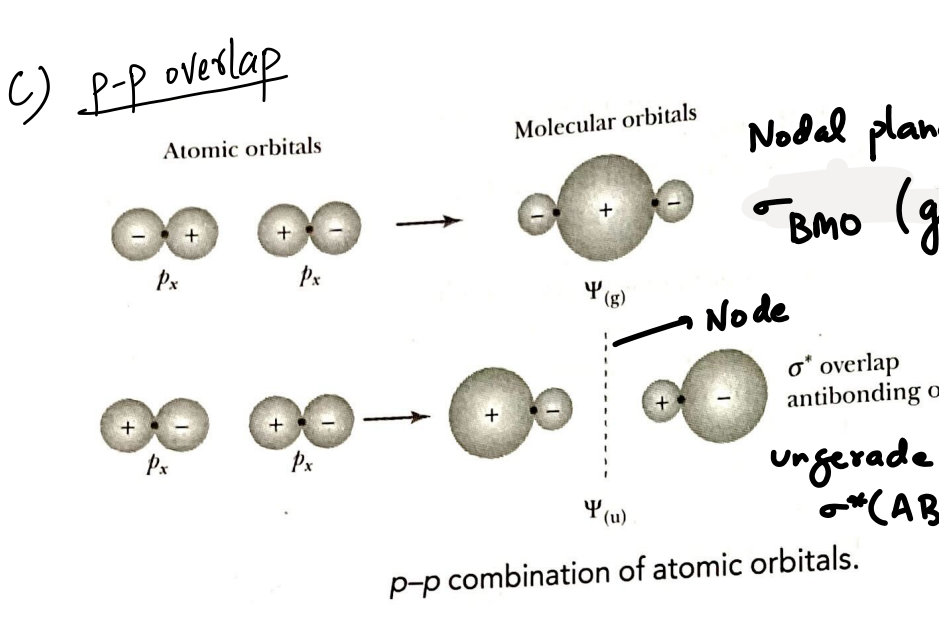
ungerade ⇒ no. of nodal plane odd ⇒ 1, 3 - - -

B) s-p overlap

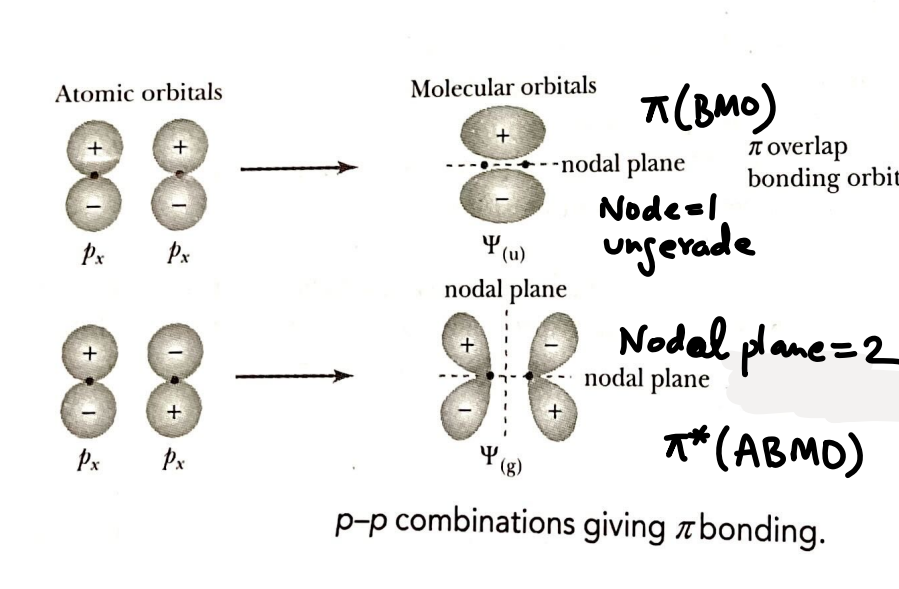


s–p combination of atomic orbitals.

C) p-p overlap

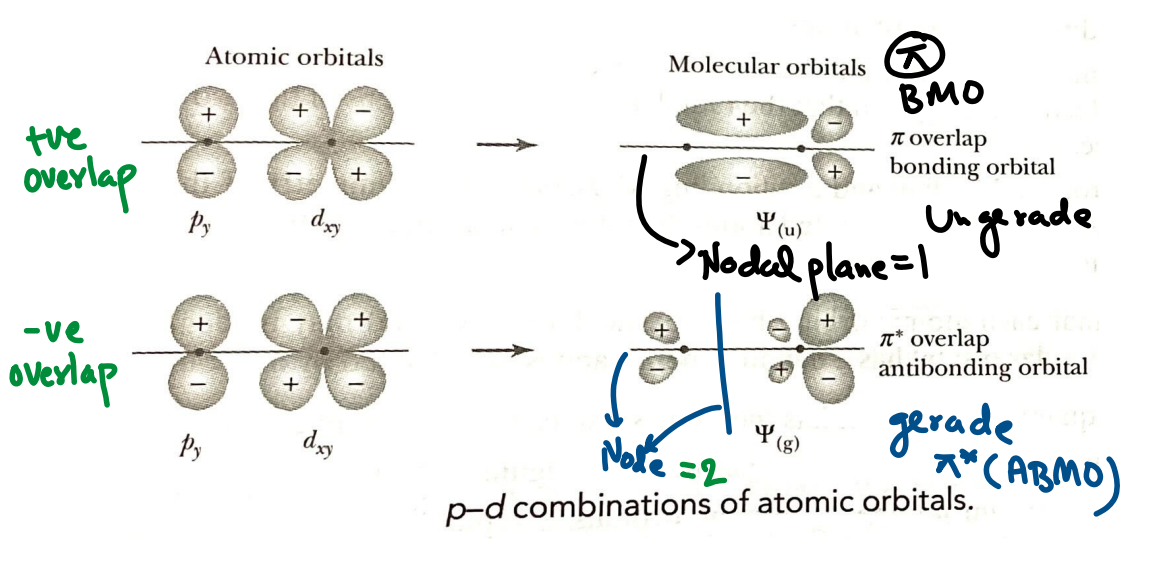


p–p combination of atomic orbitals.



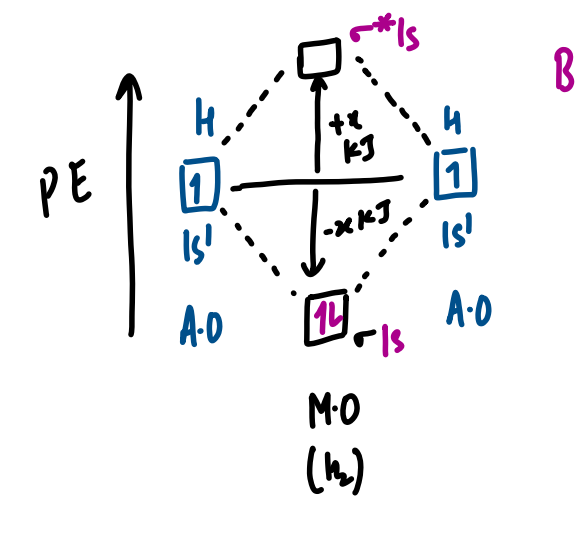
p–p combinations giving π bonding.

D) p-d overlap

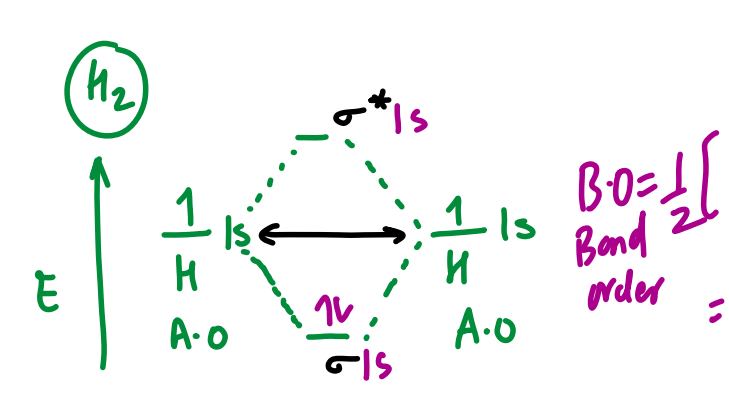


p–d combinations of atomic orbitals.

Consider H₂ formation by M.O.T

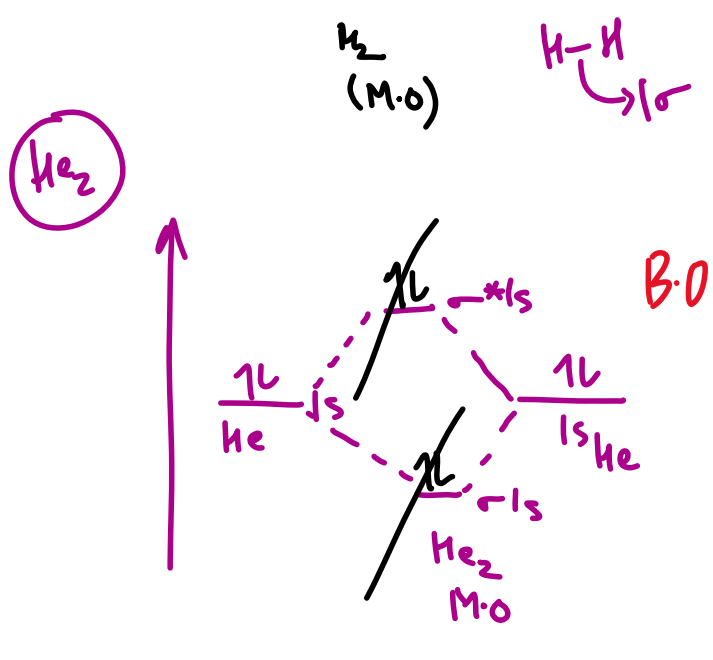


Bond order (B.O) = ½[BMO e⁻s − ABMO e⁻s] = ½[2 − 0] = 1

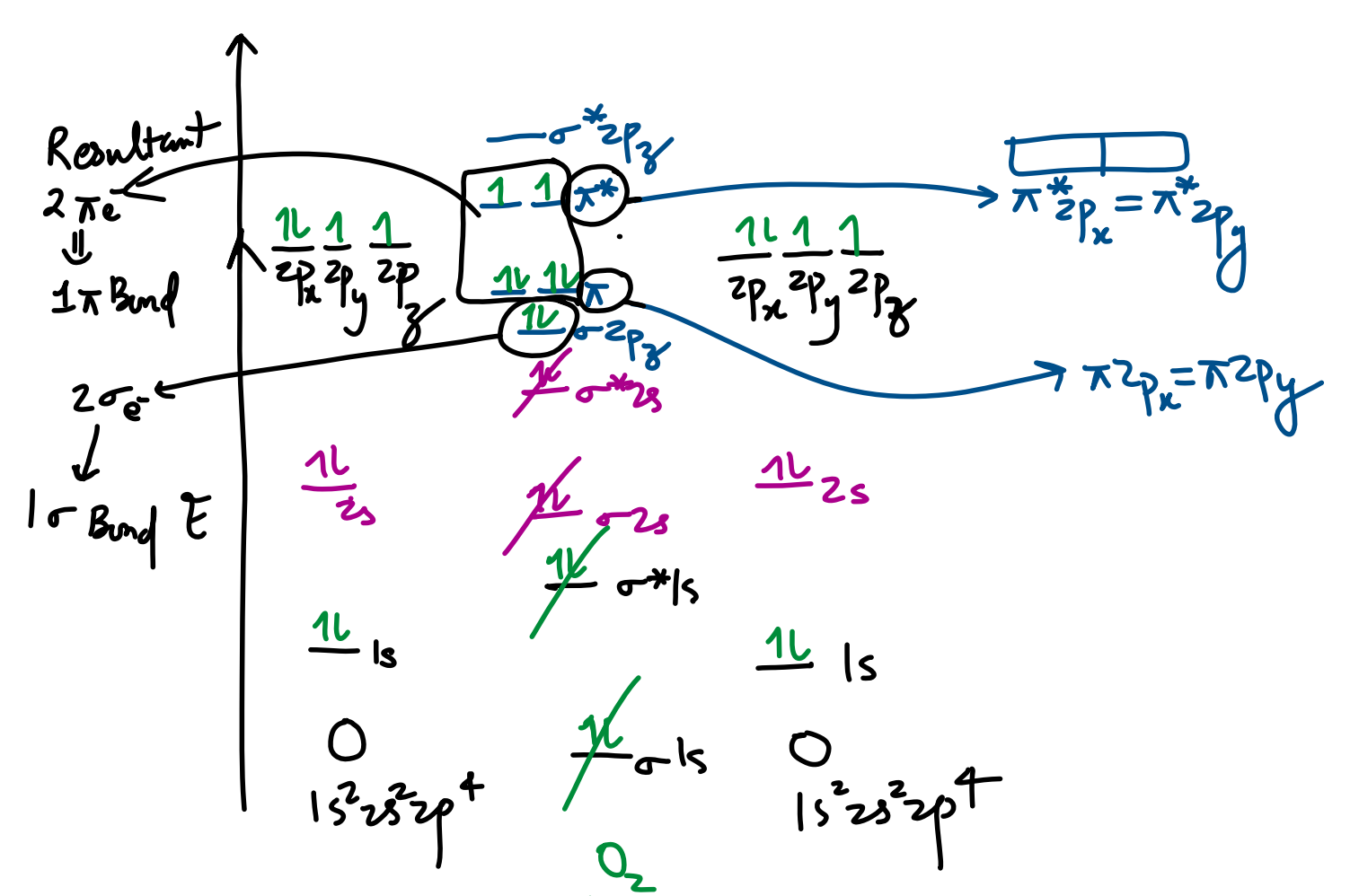


B.O (Bond order) = ½[BMO e⁻ − ABMO e⁻] = ½[2 − 0] = ①

H–H → 1σ

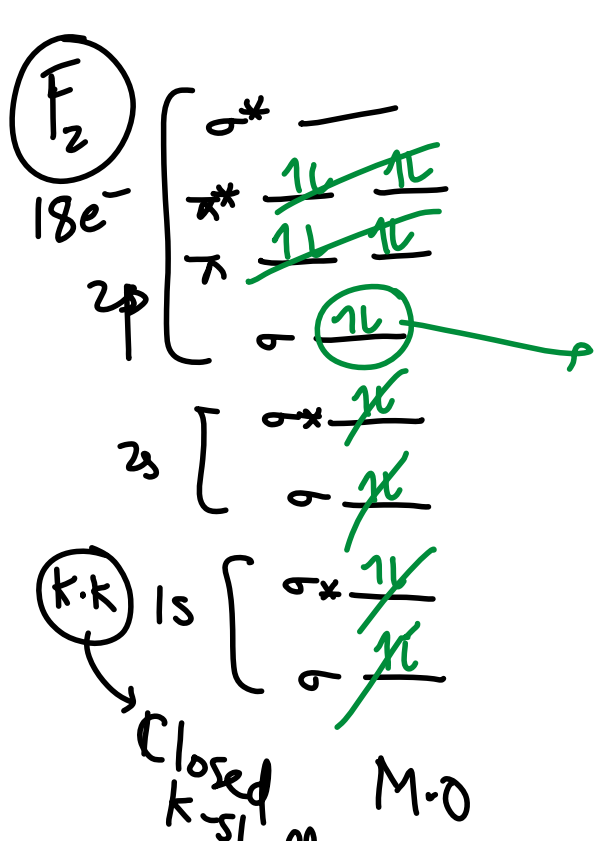


B.O(He₂) = ½(2−2) = ⓪



O $\overset{\pi}{\underset{\sigma}{=}}$ O

B.O = ½[6 − 2] = ②



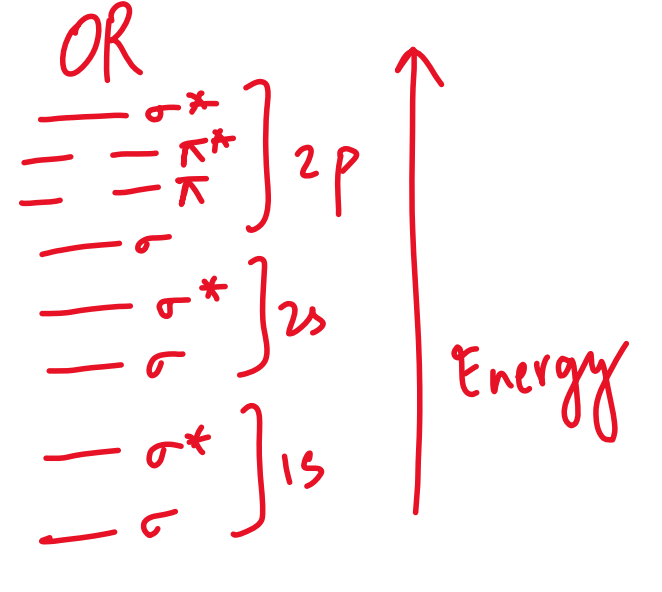
F–F (σ)

only for Diatomic molecules (Homonuclear)

① Energy order (e⁻s > 14)

σ1s < σ*1s < σ2s < σ*2s < σ2pz < π2px = π2py < π*2px = π*2py < σ*2pz

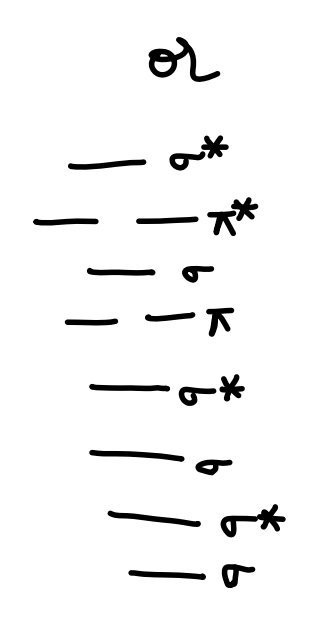
OR

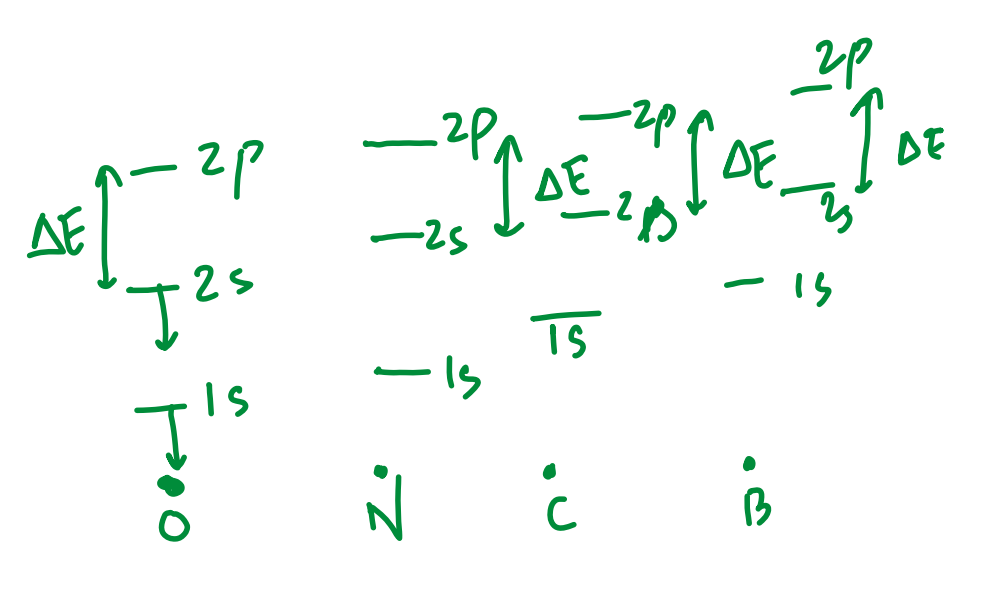


Homonuclear Diatomic Energy order e⁻s ≤ 14 → due to s-p Mixing

σ1s < σ*1s < σ2s < σ*2s < $\boxed{\pi 2p_x = \pi 2p_y < \sigma 2p_z}$ < π*2px = π*2py < σ*2pz

or

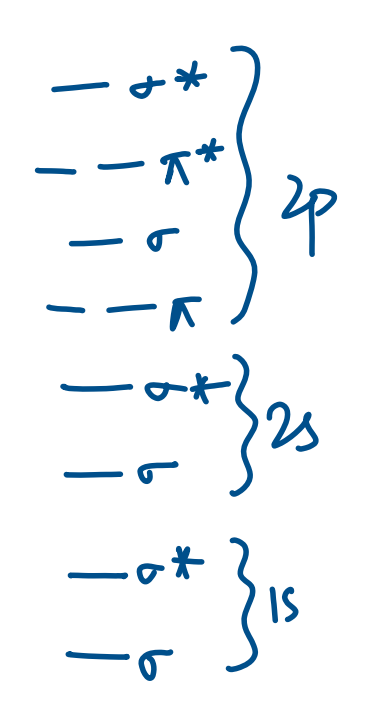




Energy order (e⁻s ≤ 14) → is obtained due to s-p Mixing

σ1s < σ*1s < σ2s < σ*2s < $\boxed{\pi 2p_x \equiv \pi 2p_y < \sigma 2p_z}$ < π*2px ≡ π*2py < σ*2pz

Or

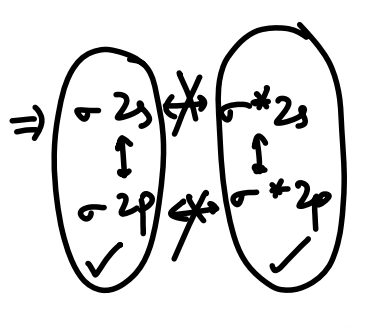


④ for s-p interaction

Same Symmetry interacts → g interacts with g, u " " u

④ Due to interaction :- M.O having less Energy will lose Energy & M.O having High " " gain Energy

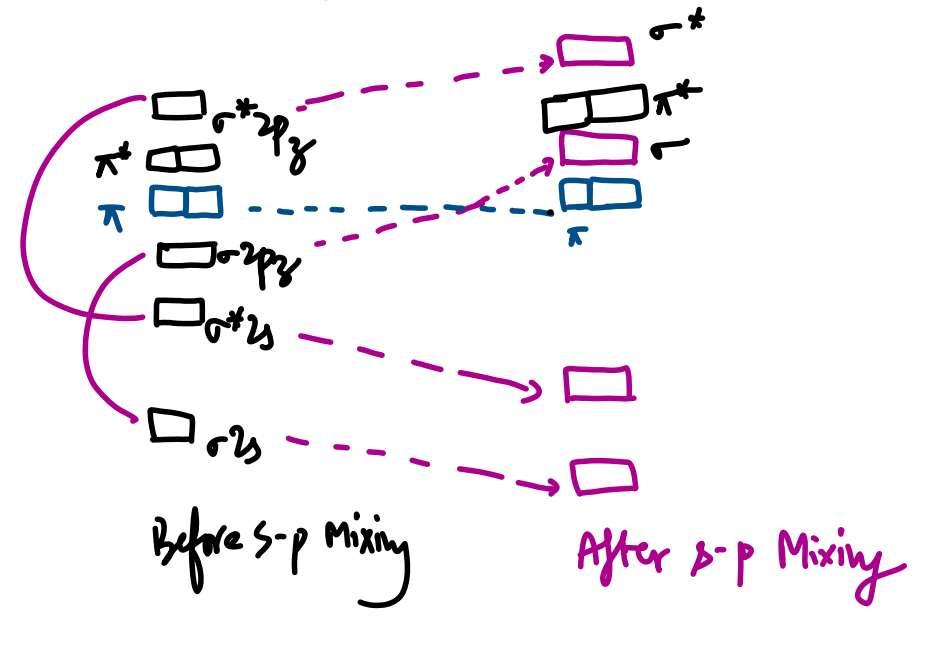
$\boxed{\text{2s-2p interaction}}$ ⇒

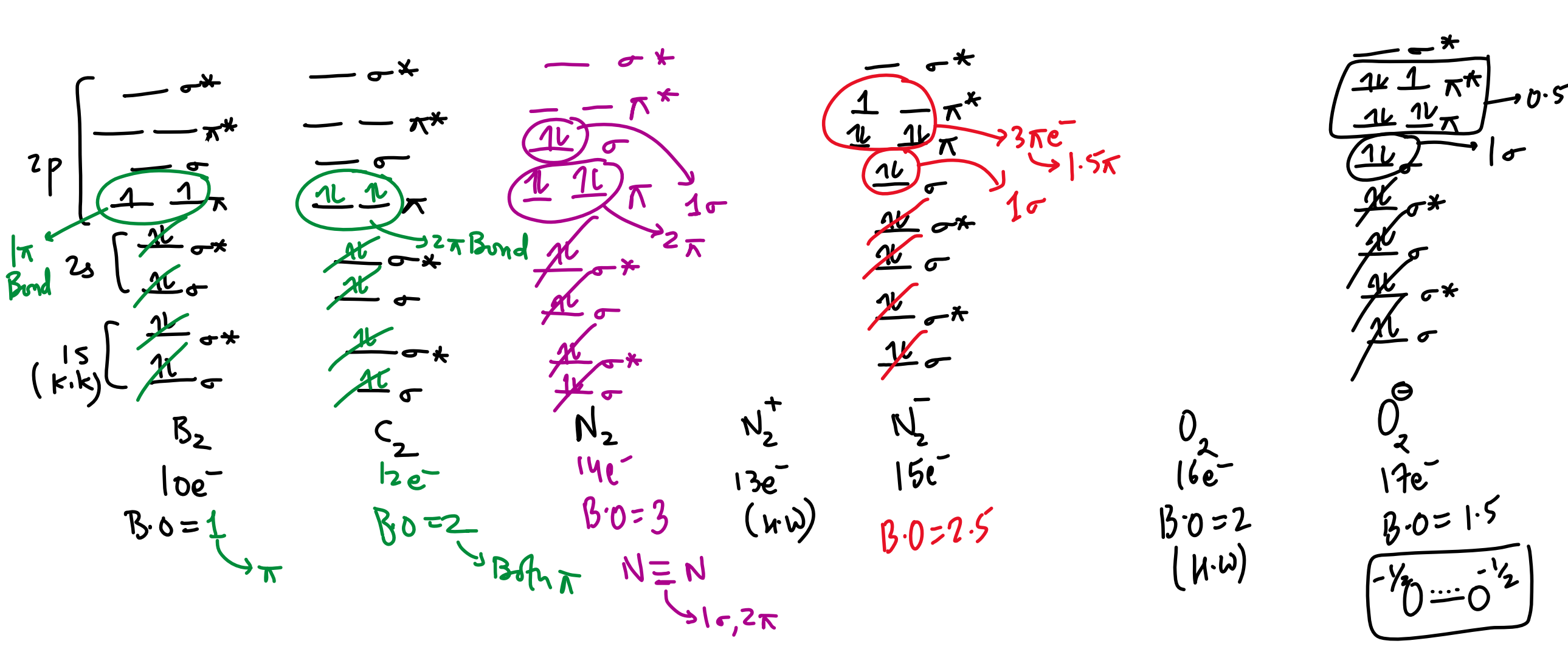


Chance of s-p interaction High

Atoms	Li	Be	B	C	N	O	F	Ne
$\Delta E_{(2p-2s)}$ in (eV)	1.8	2.8	4.5	5.3	6.0	15.0	20.5	26.7

Li > Be > B > C > N





Short trick

Total e⁻	B.O	Total e⁻	B.O
1	0.5	11	1.5
2	1	12	2
3	0.5	13	2.5
4	0	14	③ → max
5	0.5	15	2.5
6	1	16	2
7	0.5	17	1.5
8	0	18	1
9	0.5	19	0.5
10	1	20	0

O_2 → B.O = 2

N_2^+ ⇒ 2.5

N_2^- ⇒ 2.5

O_2^{2-} → 1

O_2^+ → 2.5

④ Total e⁻ even → Dia

Except (10e⁻, 16e⁻) → Para

10e⁻ → 2 unpaired e⁻ → π; 16e⁻ → 2 unpaired in π*

④ Total e⁻ odd → Para

B.O ∝ Bond strength ∝ Bond stability ∝ Bond Energy ∝ $\frac{1}{\text{Bond length}}$

④ If B.O is same, species with less antibonding e⁻ is more stable.

eg. $\boxed{N_2^+ > O_2^+}$ → stable

N_2^+ → 13e⁻, B.O = 2.5; O_2^+ → 15e⁻, B.O = 2.5

④

	e⁻s	B.O
CO	14	3
NO	15	2.5
NO^+	14	3
CN^-	14	3

$:\overset{\ominus}{C}\equiv\overset{+}{O}:$

N≡O

CO, NO⁺, CN⁻ → Isoelectronic Species

H-Bonding

F/O/N — $\overset{\delta-}{}$ — $\overset{\delta+}{H}$ ⋯⋯ $\overset{\delta-}{}$F/O/N — → Dipole-Dipole Interaction

④ $E_{Released}$ is b/w 8 to 43 kJ/mole

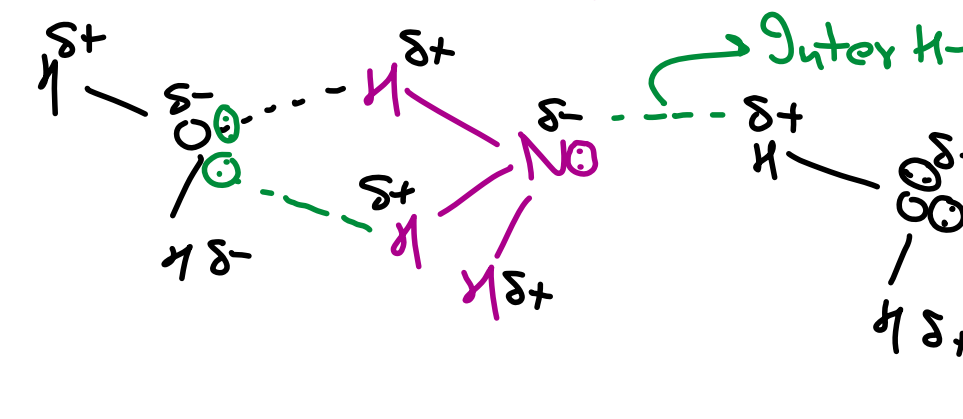
④ strength of H-Bond ∝ ΔEN

H–F⋯⋯H–F > H–O⋯⋯H–O > H–N⋯⋯H–N

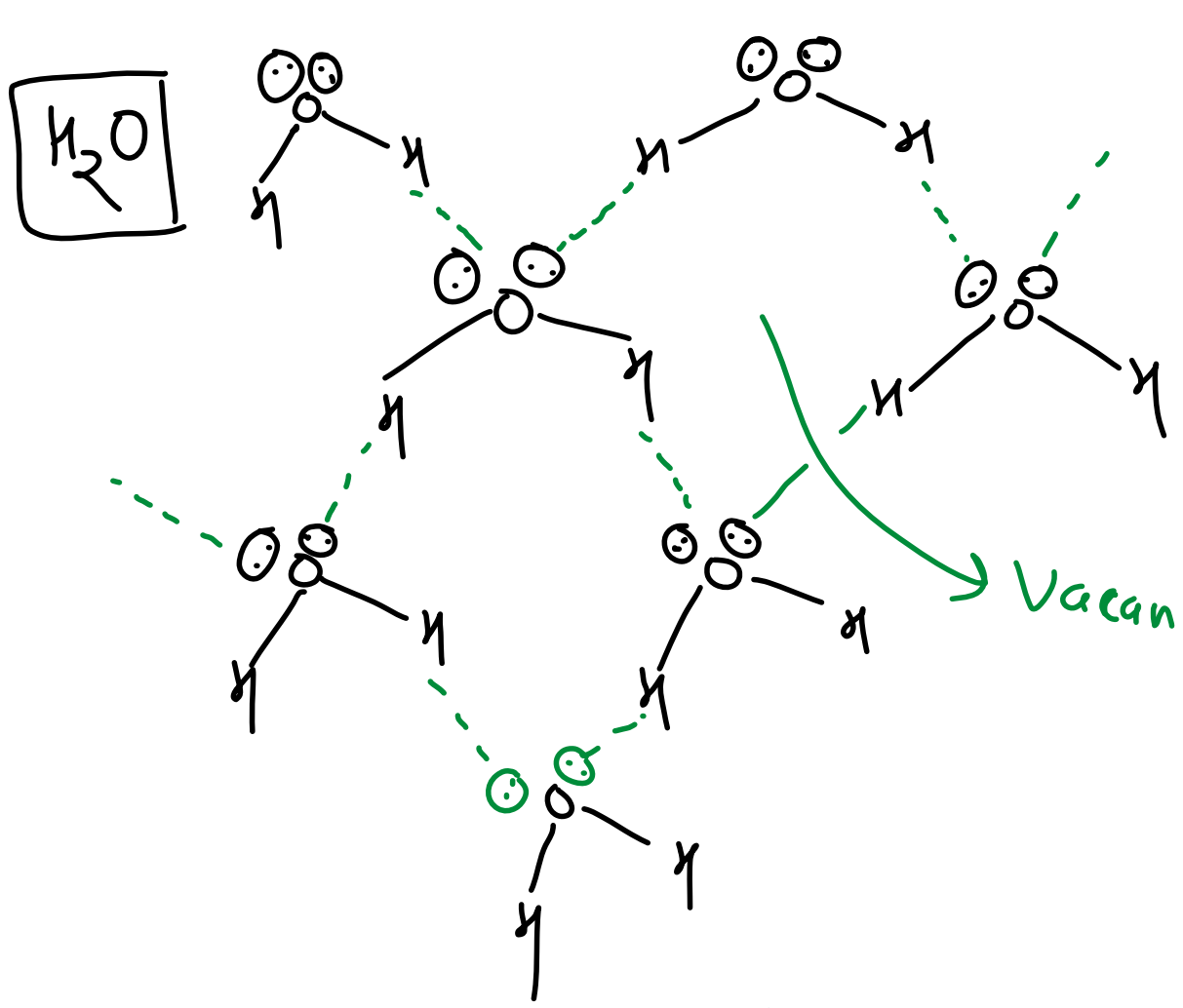
④ Type of H-Bond
- → Intermolecular H-Bond → B/w 2 molecules (Same or Different)
- → Intramolecular H-Bond → within same molecule → only feasible when 5 or 6-membered Cyclization takes place.

eg. 1) NH₃ is highly soluble in H₂O?

Solⁿ:- Because of inter H-Bond



④ $\boxed{H_2O}$



Ice (Cage like)

In a given volume

no. of H₂O molecule in Liq form > no. of molecule in Solid (ice)

mass of liq H₂O > mass of ice

So, $d_{liq\,H_2O} > d_{ice}$

so, ice floats on liq